Pyraclostrobin and Metconazole Residues in Sunflower Nectar, Pollen, and Whole Flowers

Citation:	Mack, P. 2014. Determination of residues of BAS 556 03 F in nectar, pollen, and flowers of sunflowers after one application in 2013. Study ID 701096. Performed by Eurofins Agroscience Services, EcoChem GmbH, Niefern-Öschelbronn, Germany. Sponsored by BASF SE, Ludwigshafen, Germany.
Chemicals	Pyraclostrobin and Metconazole
PC Codes:	099100, 125619
CAS #:	175013-18-0, 125116-23-6
MRID:	49459604
EPA Guideline:	Non-guideline
GLP Statement:	This study was conducted in compliance with OECD Principles of Good Laboratory Practice
Classification:	The study is classified as "**Supplemental**" and may be used quantitatively in risk assessments.
Date of Study Completion:	May 20, 2014

EPA Primary Reviewer:	Meghan Radtke, Ph.D., Biologist	Signature: Date: 4/9/15	
EPA Secondary Reviewer:	Ryan Mroz, Biologist	Signature: Date: 4/16/15	

Summary
The objective of this study was to determine residues in sunflower (*Helianthus anuus*) pollen, nectar, and whole flowers after being treated with one application of BAS 556 03 F (13% pyraclostrobin and 8% metconazole product).

In 2013, five separate locations in Europe were chosen for the study: Southern Germany (trials 1 – 3), Italy (trial 4), and Greece (trial 5). Each location had one untreated control field and a nearby field treated[1] with BAS 556 03 F at an application rate of 1.27 lb pyraclostrobin/A and 0.71 lb metconazole/A. Fields ranged from 0.04 to 0.06 ha in size. Foliar spray applications were made to flowering sunflower fields on July 17th (trial 1), August 13th (trial 2), August 22nd (trial 3), July 5th (trial 4), and July 2nd (trial 5) in 2013. No other pyraclostrobin or metconazole applications were made during the experiment or the year prior to the study.

Residue samples were collected from each plot at two time periods: within 24 hours after the application and 6 to 7 days after the application.

Pollen (0.4 g, if available) and flowerheads (12) were collected directly from the sunflower plants. Pollen was collected by beating a flowerhead against a sieve. The pollen that fell through the sieve into a bowl below it was retained for the sample. The flowerheads varied in size; they were cut into pieces and at least 1/8th of each head was retained for the residue analysis. Nectar (0.4 g, if available) was extracted using a micro-centrifuge from cut sunflower heads in the field; trial 4 did not yield enough nectar for a sample. For all samples, 12 locations were used across each plot and were pooled together for the analysis.

Samples were stored at ≤ -18°C within 12 hours of collection until analysis. Samples were shipped on blue-ice to analysis facilities: Eurofins Niefern-Öschelbronn (German sites), Eurofins Bologna (Italian site), and GAB Hellas (Greek site).

BASF method L0076/01, which determines the concentration of BAS 556 03 F by LC-MS/MS, was used to measure residues in the samples. The LOQ was 0.01 mg/kg for metconazole and pyraclostrobin. Samples were analyzed between October 29 and December 13, 2013. Percent recoveries from known spiked samples are reported in Table 1.

[1] For trial 2, the same field was used for the negative control (sampled before the foliar application) and the treatment.

Table 1. Recoveries of pyraclostrobin and metconazole. The lowest fortification level is at the LOQ.

Substrate	Fortification Level	Pyraclostrobin (%)	Metconazole (%)
Pollen	0.01 mg/kg	74.2	82.6
	0.1 mg/kg	70.9	70.5
Nectar	0.01 mg/kg	86.2	78.3
	0.1 mg/kg	79.5	72.3
Flowers	0.01 mg/kg	82.2	99.2
	0.1 mg/kg	82.8	94.6

Pyraclostrobin and metconazole residues were not detected in any of the control samples, and are thus not reported in Table 2. The highest residues were detected in pollen, with a maximum of 17 mg/kg. All residues decreased in magnitude from the initial measurement within 24 hours of application to the second sample taken 6 to 7 days later (Table 2).

Table 2. Range of pyraclostrobin and metconazole residues from treated fields

	Day After Application	**Pyraclostrobin (mg/kg)**	**Metconazole (mg/kg)**
Nectar	0 to 1	0.04 to 0.53	0.05 to 0.33
	7	<0.01	<0.01
Pollen	0 to 1	2.20 to 17.00	1.30 to 11.00
	6 to 7	0.05 to 1.3	0.03 to 0.97
Flowerheads	0 to 1	0.68 to 1.50	0.40 to 0.81
	6 to 7	0.04 to 0.32	0.03 to 0.32

Study Limitations

The residue samples were not analysed immediately, but were stored for 69 to 148 days at ≤ -18° C. Since there were no matrix spike samples associated with the sample during sample collection and storage, the residue stability is uncertain. Therefore, the study may underestimate the pyraclostrobin and metconazole residue levels because of potential degradation during the sample storage. In addition, it is uncertain if the analytical method was validated by an independent laboratory and the limit of detection (LOD) was not reported.

References

BASF Method Number L0076/01 (535/1): Method for the determination of alphacypermethrin and cypermethrin in plant matrices, 01 Feb 2005.